

Tabelle 1. Lageparameter und äquivalente isotrope Temperaturparameter (\AA^2) (Standardabweichungen in Klammern)

$$U_{\text{äq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$$

	x	y	z	$U_{\text{äq}}$
Br	0,54083 (6)	0,84124 (5)	0,62625 (5)	0,049 (1)
Cu	0,30278 (8)	0,85784 (7)	0,34875 (7)	0,063 (1)
N(11)	0,0793 (5)	0,8119 (5)	0,3670 (5)	0,044 (2)
C(12)	0,0546 (7)	0,8584 (6)	0,2830 (6)	0,047 (3)
C(13)	0,1948 (8)	0,8358 (9)	0,3147 (9)	0,066 (4)
C(14)	0,201 (1)	0,761 (1)	0,4305 (9)	0,076 (4)
C(15)	0,0700 (9)	0,708 (1)	0,5122 (8)	0,075 (4)
C(16)	0,0694 (8)	0,7367 (7)	0,4807 (6)	0,058 (4)
C(17)	0,0461 (9)	0,936 (1)	0,1523 (9)	0,071 (4)
N(21)	0,3028 (5)	0,7431 (5)	0,1577 (5)	0,045 (2)
C(22)	0,2806 (7)	0,5910 (6)	0,1278 (6)	0,044 (3)
C(23)	0,2939 (9)	0,5231 (8)	0,0022 (7)	0,063 (4)
C(24)	0,3261 (9)	0,6146 (8)	0,0978 (7)	0,068 (4)
C(25)	0,3438 (8)	0,7656 (9)	0,0688 (7)	0,060 (4)
C(26)	0,3327 (7)	0,8278 (8)	0,0589 (6)	0,053 (3)
C(27)	0,239 (1)	0,4961 (9)	0,235 (1)	0,086 (5)

Tabelle 2. Abstände (\AA) und Winkel ($^\circ$)

Die mit ' gekennzeichneten Atome befinden sich auf den symmetrie-äquivalenten Positionen $\bar{x}, \bar{y}, \bar{z}$. Die Geometrie der 2-Methylpyridin-Ringe entspricht den Erwartungswerten, die Werte sind deshalb an dieser Stelle nicht aufgeführt.

Cu—Br	2,5831 (7)	Cu—Br—Cu'	80,4 (1)
Cu—Br'	2,6045 (7)	Br—Cu—Br'	99,6 (1)
Cu—N(11)	2,022 (5)	Br—Cu—N(11)	103,4 (1)
Cu—N(21)	2,043 (5)	Br—Cu—N(21)	111,9 (1)
Cu...Cu'	3,3491 (6)	Br'—Cu—N(11)	111,5 (1)
Br...Br'	3,962 (1)	Br'—Cu—N(21)	103,7 (1)

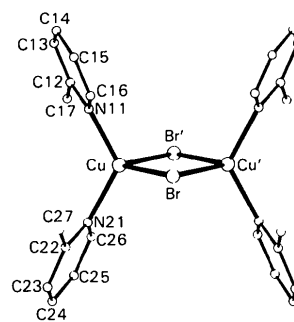


Fig. 1. Darstellung der Struktur und Atombezeichnung.

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Structure of (3RS)-4,4-Dimethyl-1-pentyn-3-yl (SR)-Methanesulfinate, $\text{C}_8\text{H}_{14}\text{O}_2\text{S}$

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Abstract. $M_r = 174.26$, monoclinic, $P2_1/n$, $a = 6.0341$ (5), $b = 11.8316$ (6), $c = 14.410$ (1) \AA , $\beta = 93.88$ (1) $^\circ$, $Z = 4$, $U = 1026.4$ (1) \AA^3 , $D_x = 1.128$ g cm^{-3} , $\mu(\text{Cu } K\alpha) = 23.5$ cm^{-1} , $T = 295$ K,

$\lambda(\text{Cu } K\alpha) = 1.5418$ \AA , $F(000) = 376$, $R = 0.038$ for 1433 reflections [$I > 2.5\sigma(I)$]. Crystals of the title compound are found to contain a racemic mixture of the (3R, SS) and (3S, SR) enantiomers. The dimethylpentynyl moiety exhibits a staggered conformation about the C(2)—C(5) bond. Molecular packing is realized through short contacts involving sulfoxo and terminal ethynyl H atoms with $\text{O}(1)\cdots\text{H}(4) = 2.28$ (1) \AA .

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Introduction. In the course of investigations concerning the stereochemical pathways of organocuprate-induced S_N2' -type reactions of 2-propynylic esters (Elsevier, Meijer, Westmijze, Vermeer & van Dijk, 1982, and references cited therein) the question arose whether the use of a chiral leaving group could influence the stereochemistry of the reaction. This paper reports on the use of a methanesulfinate group in this respect, in view of its excellent leaving character and the possibility to use it in optically active form due to the chiral sulfur center. The present study concerns the structure of one of the two (racemic) diastereomers of the methanesulfinate derived from 4,4-dimethyl-1-pentyn-3-ol that could be separated by column chromatography, in order to determine the relative stereochemistry around the optically active C and S centers. The crystals were found to contain pairs of enantiomers in a 1:1 ratio as opposed to 0.73:0.27 in the solution from which they were crystallized.

Experimental. Crystal 0.23 × 0.25 × 1.00 mm sealed in a Lindemann-glass capillary, cell constants derived from the diffractometer settings of 22 reflections ($14.5 < \theta < 15.5^\circ$), intensities collected on an Enraf-Nonius CAD-4F diffractometer, $\omega/2\theta$ -scan mode ($\theta_{\max} = 70^\circ$), Ni-filtered Cu *K* α radiation. 1959 unique reflections ($0 \leq h \leq 7$; $0 \leq k \leq 14$; $-17 \leq l \leq 17$), of which 1437 with $I > 2.5\sigma(I)$ were used in the calculations. Two reference reflections (024, $1\bar{3}2$) indicated a decay of 10% and short-term fluctuations less than 1% during the 33 h of X-ray exposure time. Lorentz-polarization and linear-decay corrections. A ψ -scan for a close-to-axial reflection (40 $\bar{2}$) showed that no correction for absorption was necessary. Structure solved by *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), H atoms located from a difference Fourier synthesis, refinement by full-matrix least-squares techniques minimizing $\sum w(\Delta F)^2$ with $w = 1$. Parameters refined: scale factor, atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms and two isotropic thermal parameters for the H atoms [one for H(2), H(4) and one for the H atoms of the methyl groups]; 144 variables. Two reflections (131, 103) probably suffering from extinction were excluded from the final calculations. Maximum shift to error on coordinates in the final cycle 0.39 [for *x* of C(6)]; anisotropic thermal parameters in the usual range; final $R = 0.038$, $wR = 0.035$, $S = 0.51$; maximum and minimum residual densities 0.07 and -0.08 e \AA^{-3} . Scattering factors from Cromer & Mann (1968) and (for H) Stewart, Davidson & Simpson (1965) corrected for anomalous-dispersion effects (Cromer & Liberman, 1970). An in-house DG Eclipse S/230 minicomputer using the programs of the *ILLIAS* package [an adaptation and extension by ALS of the *SHELX76* package (Sheldrick, 1976)], or the CDC-Cyber 175 of the University of Utrecht with

Table 1. *Final coordinates and isotropic or equivalent isotropic thermal parameters*

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} or <i>U</i> _{iso} (\AA^2)
S(1)	-0.0807 (1)	0.17375 (6)	0.60873 (4)	0.0593 (2)
O(1)	0.1157 (3)	0.1648 (2)	0.5555 (1)	0.0882 (6)
O(2)	-0.0695 (3)	0.0734 (1)	0.6857 (1)	0.0541 (4)
C(1)	-0.2969 (5)	0.1071 (3)	0.5398 (2)	0.0785 (6)
C(2)	0.0649 (4)	0.0995 (2)	0.7705 (2)	0.0501 (5)
C(3)	-0.0703 (4)	0.1608 (2)	0.8343 (2)	0.0589 (6)
C(4)	-0.1731 (5)	0.2102 (3)	0.8864 (2)	0.0802 (6)
C(5)	0.1652 (4)	-0.0113 (2)	0.8093 (2)	0.0563 (6)
C(6)	0.3142 (5)	-0.0604 (3)	0.7381 (2)	0.0920 (7)
C(7)	0.3055 (5)	0.0144 (3)	0.8988 (2)	0.0887 (7)
C(8)	-0.0179 (5)	-0.0949 (3)	0.8299 (2)	0.0785 (6)
H(2)	0.187 (1)	0.149 (1)	0.753 (1)	0.066 (1)
H(4)	-0.259 (1)	0.246 (1)	0.929 (1)	0.066 (1)
H(11)	-0.416 (1)	0.109 (1)	0.576 (1)	0.157 (1)
H(12)	-0.316 (1)	0.153 (1)	0.484 (1)	0.157 (1)
H(13)	-0.278 (1)	0.036 (1)	0.531 (1)	0.157 (1)
H(61)	0.383 (1)	-0.123 (1)	0.761 (1)	0.157 (1)
H(62)	0.247 (1)	-0.076 (1)	0.686 (1)	0.157 (1)
H(63)	0.425 (1)	-0.006 (1)	0.719 (1)	0.157 (1)
H(71)	0.219 (1)	0.048 (1)	0.948 (1)	0.157 (1)
H(72)	0.368 (1)	-0.050 (1)	0.927 (1)	0.157 (1)
H(73)	0.393 (1)	0.069 (1)	0.894 (1)	0.157 (1)
H(81)	-0.104 (1)	-0.115 (1)	0.774 (1)	0.157 (1)
H(82)	0.037 (1)	-0.166 (1)	0.855 (1)	0.157 (1)
H(83)	-0.109 (1)	-0.064 (1)	0.877 (1)	0.157 (1)

Table 2. *Bond distances (\AA), angles ($^\circ$) and torsion angles ($^\circ$)*

S(1)-O(1)	1.458 (2)	C(1)-H(13)	0.86 (2)
S(1)-O(2)	1.623 (2)	C(2)-H(2)	0.98 (1)
S(1)-C(1)	1.771 (3)	C(4)-H(4)	0.94 (1)
O(2)-C(2)	1.453 (3)	C(6)-H(61)	0.90 (1)
C(2)-C(3)	1.463 (3)	C(6)-H(62)	0.85 (2)
C(2)-C(5)	1.533 (4)	C(6)-H(63)	0.98 (1)
C(3)-C(4)	1.162 (4)	C(7)-H(71)	0.99 (2)
C(5)-C(7)	1.525 (4)	C(7)-H(72)	0.93 (2)
C(5)-C(6)	1.524 (4)	C(7)-H(73)	0.84 (1)
C(5)-C(8)	1.527 (4)	C(8)-H(81)	0.95 (2)
C(1)-H(12)	0.97 (2)	C(8)-H(82)	0.96 (2)
C(1)-H(11)	0.92 (1)	C(8)-H(83)	0.97 (2)
O(1)-S(1)-O(2)	108.0 (1)	C(3)-C(2)-H(2)	108.9 (8)
O(1)-S(1)-C(1)	105.5 (1)	C(5)-C(2)-H(2)	108.2 (7)
O(2)-S(1)-C(1)	93.0 (1)	C(3)-C(4)-H(4)	177.0 (9)
S(1)-O(2)-C(2)	114.5 (1)	C(5)-C(6)-H(61)	110 (1)
O(2)-C(2)-C(5)	108.0 (2)	C(5)-C(6)-H(62)	114.4 (8)
C(3)-C(2)-C(5)	114.8 (2)	C(5)-C(6)-H(63)	112 (1)
O(2)-C(2)-C(3)	109.3 (2)	H(61)-C(6)-H(62)	109 (1)
C(2)-C(3)-C(4)	178.3 (3)	H(61)-C(6)-H(63)	110 (1)
C(2)-C(5)-C(8)	110.6 (2)	H(62)-C(6)-H(63)	101 (1)
C(7)-C(5)-C(8)	109.4 (2)	C(5)-C(7)-H(71)	113.2 (8)
C(6)-C(5)-C(8)	110.6 (2)	C(5)-C(7)-H(72)	113 (1)
C(2)-C(5)-C(7)	108.7 (2)	C(5)-C(7)-H(73)	113 (1)
C(2)-C(5)-C(6)	108.5 (2)	H(71)-C(7)-H(72)	104 (1)
C(6)-C(5)-C(7)	109.1 (2)	H(71)-C(7)-H(73)	97 (1)
S(1)-C(1)-H(13)	114.5 (8)	H(72)-C(7)-H(73)	115 (1)
S(1)-C(1)-H(11)	104 (1)	C(5)-C(8)-H(81)	110.9 (9)
H(12)-C(1)-H(13)	116 (2)	C(5)-C(8)-H(82)	113.9 (6)
S(1)-C(1)-H(12)	105.1 (8)	C(5)-C(8)-H(83)	110.1 (8)
H(11)-C(1)-H(12)	114 (1)	H(81)-C(8)-H(82)	104 (1)
H(11)-C(1)-H(13)	103 (1)	H(81)-C(8)-H(83)	112 (1)
O(2)-C(2)-H(2)	107.5 (9)	H(82)-C(8)-H(83)	105 (1)
O(1)-S(1)-O(2)-C(2)	83.5 (2)	S(1)-O(2)-C(2)-C(3)	85.4 (2)
C(1)-S(1)-O(2)-C(2)	-169.2 (2)	S(1)-O(2)-C(2)-C(5)	-149.2 (1)

programs of the *EUCLID* package [calculation of geometrical data and preparation of illustrations (Spek, 1982)] were used.

Discussion. Final atomic parameters are given in Table 1.* Bond distances, angles and selected torsion angles describing the conformation of the molecule are listed in Table 2. A *PLUTO* drawing (Motherwell & Clegg, 1978; Spek, 1982) of the molecule along with the numbering adopted is shown in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39555 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

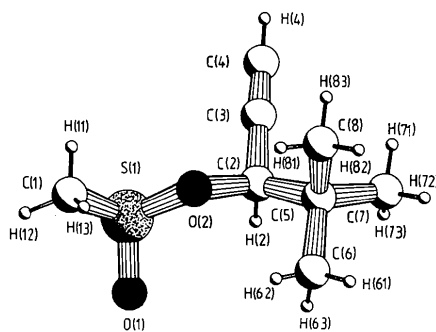


Fig. 1. Drawing of the (3*R*, *SS*) enantiomer with the numbering scheme adopted.

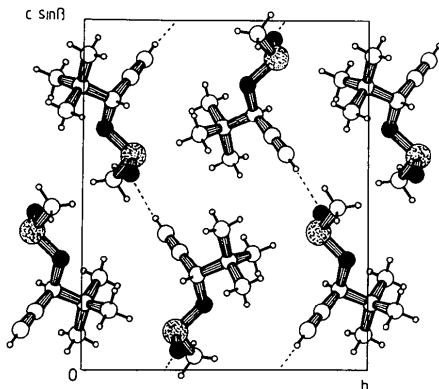


Fig. 2. Projection of the structure down the *a* axis illustrating the short C(4)–H(4)···O(1) interactions that link the two enantiomers into infinite chains running in the $[\bar{1}01]$ direction. O atoms are represented by black spheres and S atoms by stippled spheres.

The title molecule possesses chiral carbon, C(2), and sulfur atoms. Among the four possible stereoisomers, two enantiomers occur in equal number in the centrosymmetric unit cell, thus constituting a racemic crystal. Bond distances and angles correspond to the values required by the atom type and hybridization. A sterically favorable conformation with *trans* orientation of the ethynyl and S=O moieties with respect to the plane through S(1)–O(2)–C(2) occurs in the crystal-line state.

The lone pair on sulfur is positioned *cis* to the ethynyl group. The dimethylpentynyl residue exhibits a staggered conformation with torsion angles about the C(2)–C(5) bond close to 60° [57.4 (3)–62.7 (3)°]. The crystal structure is composed of discrete molecules that are separated by van der Waals distances, except for a short intermolecular contact involving the terminal ethynyl hydrogen and S=O oxygen atom of the sulfinate group [H(4)···O(1') = 2.28 (1) Å; \angle C–H···O = 165.2 (9) and \angle H···O–S = 135.4 (3)°; (i) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$], that is significantly shorter than the sum of the van der Waals radii [O 1.40, H 1.20 Å (Pauling, 1960)], suggesting a significant interaction of the type C–H···O–S (Fig. 2).

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